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EUROPEAN PATENT APPLICATION

⑰ Application number: 80304646.5

⑱ Date of filing: 19.12.80

⑥ Int. Cl.³: **B 01 J 37/00, B 01 J 37/04,**
C 10 G 35/14, C 10 G 35/085

⑳ Priority: 26.12.79 US 106494

④③ Date of publication of application: 08.07.81
Bulletin 81/27

⑧④ Designated Contracting States: DE FR GB IT NL

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⑤④ Preparation of magnetic catalysts, and hydrocarbon reforming process using the magnetic catalyst.

⑤⑦ A method for the preparation of a magnetic catalyst, particularly a magnetic reforming catalyst, in which a Group VIII noble metal is incorporated within an inorganic oxide particulate mass, suitably by impregnation of preformed particles comprising the inorganic oxide. The metal-containing inorganic oxide particulate mass, in the desired proportion, is then admixed with magnetic alloy particles (notably iron alloy or cobalt alloy) and an inorganic oxide precursor which serves as a binder, to form a particulate composite mass comprised of particles of magnetic alloy dispersed as inclusions within an inorganic oxide matrix. The particulate composite mass is dried and fired. The method of preparation avoids plating out of the noble metal on the magnetic alloy.

When used in a reforming process, particles of the catalyst are fluidized in a bed by a hydrocarbon feed and hydrogen while being subjected to an applied magnetic field which stabilizes the fluidized bed.

EP 0 031 700 A1

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Preparation of Magnetic Catalysts, and Hydrocarbon
Reforming Process Using the Magnetic Catalyst

2 Catalytic reforming, or hydroforming, is a well
3 established industrial process employed by the petroleum
4 industry for improving the octane quality of naphthas or
5 straight run gasolines. In reforming, a multi-functional
6 catalyst is employed which contains a metal hydrogenation-
7 dehydrogenation (hydrogen transfer) component, or compon-
8 ents, substantially atomically dispersed upon the surface
9 of a porous, inorganic oxide support, notably alumina.
10 Noble metal catalysts, notably platinum, have been widely
11 used commercially in recent years in the production of
12 reforming catalysts, and platinum on alumina catalysts
13 have been commercially employed in refineries for the last
14 few decades. In the last decade, additional metallic com-
15 ponents have been added to platinum as promoters to further
16 improve the activity or selectivity, or both, of the basic
17 platinum catalyst, e.g., iridium, rhenium, tin, and the
18 like.

19 In recent months considerable thought has been
20 given to improving reforming processes, particularly by
21 providing short cycle processes which, inter alia, utilize
22 beds of fluidizable magnetizable catalytic particles which
23 are contacted, and fluidized, with a naphtha feed and hy-
24 drogen at reforming conditions to produce a naphtha product
25 of improved octane while simultaneously the fluidized beds
26 are subjected to an axially applied magnetic field. In
27 such processes the activity and selectivity of the catalyst
28 throughout the operation approximates that of fresh, or
29 freshly-reactivated catalyst, and preferably the operation
30 is conducted at high severity conditions, as contrasted
31 with present commercially produced reforming operations.
32 In the improved processes, continuous operation of all
33 portions of the reforming unit is conducted, and the
34 catalyst is moved therethrough as a more cohesive phase,
35 or phase of narrow age distribution. Such processes are
36 admirably suitable for conducting operations with a wide
37 variety of feeds, particularly at high temperatures

1 and low pressures, or other high severity conditions.

2 The application of a magnetic field upon a bed
3 of fluidized, magnetizable catalytic particles in its pre-
4 ferred aspects stabilizes the bed and thereby suppresses,
5 or minimizes bubble formation. The characteristics attrib-
6 uted to the stabilized bed greatly improve gas-solids
7 contacting and lessen the need for long residence times;
8 and yet the state of the bed is such that it can be rapidly
9 recycled between reactor and regenerator. The properties
10 of the bed in a magnetically stabilized state approach
11 those of plug flow, thus providing the higher gas-solids
12 contacting efficiencies offered by fixed bed contacting.
13 Yet the magnetically stabilized bed, since it is fluidized,
14 offers the advantages of fluidized beds for purposes of
15 transport. Shorter contact times become feasible, and
16 desirable because of higher average catalyst activity
17 level. Moreover, the small particles which in a fixed
18 bed would have a prohibitively high pressure drop at reason-
19 able gas velocities provide very large surface areas which
20 enhance catalysis and gas-solids contacting.

21 The catalyst employed in a magnetically stabil-
22 ized bed operation is necessarily constituted of composite
23 particles, preferably small particles, suitably particles
24 which range in average diameter below about 800 microns,
25 more preferably those which range from about 100 to 300
26 microns. The particles contain, besides a carrier or
27 support material, a sufficient amount of a ferromagnetic
28 or ferrimagnetic material to make the particles magnetizable,
29 and a hydrogenation-dehydrogenation component, or components.
30 A reforming catalyst also contains a halide component and,
31 preferably, the catalyst is sulfided. Preferred magnetiz-
32 able materials include ferromagnetic and ferrimagnetic
33 alloys of metals, and metallic metals such as iron, nickel,
34 cobalt. In general, also, the non-magnetizable material
35 will include a vast number of conventional materials
36 which are inert and/or known to catalyze the desired reac-
37 tion.

1 The magnetizable component can be directly in-
2 corporated with the non-magnetizable material. For
3 example, the non-magnetizable materials may be impregnated
4 with a soluble precursor of a ferromagnetic or ferrimagnetic
5 substance, e.g., an oxide, which is subsequently reduced
6 to render the particles ferromagnetic or ferrimagnetic.
7 Alternatively, the ferromagnetic or ferrimagnetic material
8 may be incorporated into the non-magnetizable component by
9 encapsulation of finely divided ferromagnetic or ferri-
10 magnetic material. Thereafter, the catalytic component,
11 e.g., the Group VIII noble metal, or metals, (Periodic
12 Table of the Elements; Sargent Welch Scientific Company,
13 Copyright 1968) notably platinum and metals used as pro-
14 motors, if any, are composited with a previously pilled,
15 pelleted, beaded, or extruded particulate support material
16 by the impregnation method. Pursuant to the impregnation
17 method, porous refractory inorganic oxides in dry or
18 solvated state are contacted, either alone or admixed, or
19 otherwise incorporated with a metal or metals-containing
20 solution, or solutions, and thereby impregnated by either
21 the "incipient wetness" technique, or a technique embodying
22 absorption from a dilute or concentrated solution, or solu-
23 tions, with subsequent filtration or evaporation to effect
24 total uptake of the metallic components. Unfortunately,
25 however, it is found that during impregnation of the
26 catalytic metals onto the carriers, or supports, signifi-
27 cant portions thereof are often lost or rendered cata-
28 lytically inactive, or ineffective, apparently because the
29 metals plate out on the ferromagnetic alloys or metals.

30 Only iron and cobalt, or alloys of such metals
31 have sufficiently high Curie temperatures to remain magne-
32 tic in high temperature operations, notably at the high
33 process temperatures used in refining operations. Unfortu-
34 nately too, only a few alloys of these metals are suffi-
35 ciently passive that they can withstand attack by the
36 liquids and gases of process streams; such attack often
37 causing the metal alloys to become rapidly oxidized, this

1 resulting in the loss of their magnetic character. Of the
2 handful of metal alloys which are suitable for this purpose,
3 e.g., stainless steel alloys, an unacceptable amount of
4 the catalytic metal, e.g., Group VIII noble metal, notably
5 platinum, is deposited on the alloy particles, the deposit-
6 ed catalytic metal being rendered ineffective in the per-
7 formance of its catalytic function and thereby wasted.
8 Such waste is obviously burdensome, and often intolerable.

9 It is accordingly a primary objective of the
10 present invention to provide a novel composition, and process
11 for the preparation of magnetic, catalytic composites to
12 improve catalytic metals utilization.

13 A particular object is to provide a process of
14 such character wherein magnetic ferrous metal alloy and
15 catalytic metal components are incorporated as a part of said
16 magnetic, catalytic composites without loss of the catalytic
17 metals utilization.

18 A more particular object is to provide a process
19 of said character for improving the catalytic effectiveness
20 of the catalytic metal components added to said composites,
21 especially Group VIII noble metals, notably platinum, which
22 is incorporated with said composites.

23 These objects and others are achieved in accord-
24 ance with the practice of the present invention which
25 embodies a composition, and process wherein a Group VIII
26 noble metal is incorporated within an inorganic oxide
27 particulate mass, said inorganic oxide particulate mass
28 is then admixed with magnetic alloy particles and an in-
29 organic oxide precursor which serves as a binder, and
30 the admixture is formed into a particulate composite mass
31 characterized as magnetic alloy particles dispersed as
32 inclusion within an inorganic oxide matrix.

33 Generally, in the practice of this invention,
34 a portion of inorganic oxide particles, notably alumina,
35 is contacted with a solution which contains a compound,
36 or compounds, of a Group VIII noble metal, notably platinum,
37 which is deposited within the composite particle in cata-
38 lytically effective amounts. The noble metal, or noble

1 metals-containing particulate portion, is then admixed or
2 otherwise incorporated with magnetic alloy-particles
3 and an inorganic oxide precursor, notably an alumina pre-
4 cursor, which acts as a binder to form composite particles
5 containing said catalytic metal, or metals, and the magne-
6 tic alloy particles, the latter as inclusions within an
7 inorganic oxide, or alumina matrix. By performing a cata-
8 lyst, and then compositing said catalyst with magnetic
9 alloy particles in this manner, the catalytic metals are
10 in effect added to the total particulate mass in the de-
11 sired quantity without significant loss of the catalytic
12 metal as would normally be occasioned by the surface de-
13 position of the catalytic metal upon said particulate
14 magnetic alloy inclusions.

15 In its preferred aspects, a portion of catalyst
16 is preformed in a conventional manner, suitably by
17 cogelling catalytically effective amounts of a catalytic
18 metal, or metals, with alumina, or by impregnation of pre-
19 formed alumina particles by contact with a solution, or
20 solutions, of catalytically effective amounts of said
21 metal, or metals. The portion of catalyst is then admixed
22 with the desired amount of a particulate magnetic alloy,
23 notably a particulate magnetic alloy of iron or cobalt,
24 especially a magnetic stainless steel alloy, and sufficient
25 of an aluminum oxide precursor solution, or solution which
26 contains a hydrous form of alumina and a neutralizing agent,
27 to congeal and serve as a binder for the occluded catalytic
28 particles and magnetic alloy particles. The admixture of
29 catalyst, aluminum oxide precursor and magnetic alloy
30 particles can be congealed by various known catalyst pre-
31 paration techniques, especially spheroiding techniques,
32 extrusion and spray drying being preferred.

33 The portion of preformed catalyst is made from
34 a mass of particulate alumina of very small particle size,
35 and in its preferred aspects the particulate alumina is of
36 average particle size ranging below about 150 microns,
37 preferably from about 1 to 150 microns, more preferably

1 from about 1 to about 50 microns. The small particle
2 sizes provide considerably greater crush strength in the
3 finished catalyst than provided by particles of relatively
4 large size, which is particularly important in that the
5 overall strength of the catalyst is lessened by the
6 necessary addition of the particulate magnetic alloy.
7 The mass of particulate alumina is impregnated with a solu-
8 tion, or solutions, containing a salt, or salts, of the
9 catalytic metal, or metals, and the portion of catalyst
10 is then dried and calcined. The portion of metals-contain-
11 ing catalyst is provided with sufficient of the hydrogen-
12 ation component to provide the desired amount of metal, or
13 metals, on the finished catalyst, this of course taking
14 into account the amount of binder, calculated on a dry
15 basis, and the amount of the inclusions. The finished
16 catalyst, exclusive of the added alloy component, generally
17 contains from about 0.01 percent to about 3 percent, pre-
18 ferably from about 0.2 percent to about 1 percent, of the
19 catalytic metal, or metals (dry basis). This means,
20 of course, that sufficient metal is added to the initial
21 portion of the catalyst such that when it is combined with
22 the binder, and thereby diluted, the finished catalyst
23 will nonetheless contain the desired concentration of the
24 metal. For example, if it is desired to produce a finished
25 catalyst which contains 0.6 weight percent platinum (dry
26 basis), then one would mix a portion of catalyst which
27 contained 1.2 weight percent platinum (dry basis) with an
28 equal weight of an aluminum oxide precursor (dry basis) to
29 provide a finished catalyst containing the desired 0.6
30 weight percent platinum (dry basis), exclusive of the weight
31 of the alloy particles. Or, one would mix a portion of
32 catalyst which contained 1.2 weight percent platinum (dry
33 basis) twice the weight of the aluminum oxide precursor
34 (dry basis) to obtain a finished catalyst containing 0.4
35 weight percent platinum (dry basis), exclusive of the
36 weight of alloy particles.

37 The catalyst portion is admixed with magnetic

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1 alloy particles of very small particle size, generally of
2 average diameter ranging from about 5 microns to about 150
3 microns, preferably from about 10 microns to about 44
4 microns. Sufficient of the magnetic alloy particles and
5 aluminum oxide precursor is used to provide composite
6 particles which contain from about 0.05 percent to about
7 50 percent, preferably from about 5 percent to about 40
8 percent, based on total catalyst volume (dry basis), of
9 the magnetic alloy particles, or from about 10 percent to
10 about 80 percent, preferably from about 20 percent to
11 about 60 percent, based on the weight of total catalyst
12 (dry basis). In general, the finished composite catalyst
13 contains from about 10 percent to about 40 percent, pre-
14 ferably from about 25 percent to about 35 percent, of
15 the hydrogenation-dehydrogenation/inorganic oxide, or
16 alumina component, from about 10 percent to about 40
17 percent, preferably from about 25 percent to about 35
18 percent, of the inorganic oxide, or alumina component
19 added as a gel, and from about 20 percent to about 60
20 percent, preferably from about 30 percent to about 50
21 percent, of the magnetic alloy particles component, based
22 on the total weight of the catalyst (dry basis). The com-
23 posite catalyst is dried and calcined, and the catalytic
24 metal, or metals, which may be agglomerated during calcina-
25 tion or spray drying, is readily redispersed by halogen
26 treatment in conventional manner.

27 Plating out of the catalytic metal, or metals,
28 upon said alloy particles component is avoided by predisper-
29 sion of catalytically effective amounts of the catalytic
30 metal, or metals, throughout a support material prior to
31 incorporation of the magnetic alloy particles within the
32 composite. In the present process, the catalytic effect-
33 iveness of the metal, or metals, is the same, or essentially
34 the same, as would be obtained in a catalyst otherwise
35 similar in composition, and similarly prepared, exclusive
36 of the presence of the particulate magnetic alloy component.
37 Albeit the catalytic metal, or metals of the catalyst

1 composite are agglomerated, e.g., during use, while
2 drying or on calcination at high temperature in the pres-
3 ence of an agglomerating atmosphere, the agglomeration
4 and nature of the agglomeration is the same, or essentially
5 the same, as would be expected in ordinary catalyst prepara-
6 tion, and use, and the catalytic metal, or metals, are
7 readily redispersed in conventional manner. The phenomenon
8 thus differs from the loss normally experienced with that of
9 depositing the catalytic metal, or metals, on a particle
10 containing the particulate magnetic alloy component wherein
11 the effectiveness of the catalytic metal, or metals, is
12 lessened, or lost as apparently occasioned by plating out
13 of some of the catalytic metal, or metals, upon the
14 particulate magnetic alloy component.

15 The catalyst employed in accordance with this
16 invention is thus necessarily constituted of composite
17 particles which contain a carrier or support material,
18 sufficient amounts of the particulate magnetic alloy to
19 make the composite particles magnetizable, and a cata-
20 lytically effective amount of a Group VIII noble metal, or
21 metals component, or components. It also includes a halide
22 component and, the catalyst may be sulfided. The first
23 step in the preparation of the catalyst requires the pre-
24 paration of a catalyst which is conventional and convention-
25 ally prepared in all respects. A porous, refractory
26 inorganic oxide, particularly alumina, is employed as a
27 carrier material, or support. The support can contain,
28 e.g., one or more of alumina, bentonite, clay, diatomaceous
29 earth, zeolite, silica, activated carbon, magnesia, zir-
30 conia, thoria, and the like; though the most preferred
31 support is alumina to which, if desired, can be added a
32 suitable amount of other refractory carrier materials such
33 as silica, zirconia, magnesia, titania, etc., usually in
34 a range of about 1 to 20 percent, based on the weight of
35 the support. A preferred support for the practice of the
36 present invention is one having a surface area of more than
37 $50 \text{ m}^2/\text{g}$, preferably from about 100 to about $300 \text{ m}^2/\text{g}$, a

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1 bulk density of about 0.3 to 1.0 g/ml, preferably about 0.4
2 to 0.8 g/ml, an average pore volume of about 0.2 to 1.1
3 ml/g, preferably about 0.3 to 0.8 ml/g, and an average pore
4 diameter of about 30 to 300Å.

5 The Group VIII metal hydrogenation-dehydrogenation
6 component, or components, can be composited or intimately
7 associated with the porous inorganic oxide, alumina support
8 or carrier by various techniques known in the art such as
9 ion-exchange, coprecipitation with the alumina in the sol
10 or gel form, and the like. For example, the catalyst com-
11 posite can be formed by adding together suitable reagents
12 such as salt of platinum and ammonium hydroxide or carbonate,
13 and a salt of aluminum such as aluminum chloride or aluminum
14 sulfate to form aluminum hydroxide. The aluminum hydroxide
15 containing the salts of platinum can then be heated, dried,
16 formed into pellets or extruded, and then calcined in
17 nitrogen or other non-agglomerating atmosphere. The metal
18 hydrogenation components can also be added to the catalyst
19 by impregnation, typically via an "incipient wetness"
20 technique which requires a minimum of solution so that the
21 total solution is absorbed, initially or after some
22 evaporation. Impregnation onto the support by the absorp-
23 tion method is preferred.

24 Various metals from the Group VIII noble metals
25 can be composited with the support, usually as an element,
26 or a compound or salt of an element of such group (Periodic
27 Table of the Elements; Sargent Welch Scientific Company,
28 Copyright 1968). Exemplary of the Group VIII metal
29 hydrogenation-dehydrogenation metals are palladium, rhodium,
30 ruthenium, iridium, osmium and platinum, platinum being a
31 highly preferred component. Promoters can be added, if
32 desired. Such promoters can include suitably a component
33 selected from the Group IV metals, Group VI metals, Group
34 VII metals, and Group VIII metals. For example, germanium,
35 tin, lead, osmium, ruthenium, or rhodium can be used, and
36 iridium or rhenium, or both, are preferred. Although one
37 or more of these components can be added by any of the

1 conventional methods, it is preferable to add them by
2 impregnation prior to, following or simultaneously with the
3 impregnation of the noble metal.

4 It is generally preferred to deposit the Group
5 VIII noble metal, or metals, and metals used as promoters,
6 if any, on a powdered particulate support material by the
7 impregnation method. Pursuant to the impregnation method,
8 porous refractory inorganic oxides in dry or solvated
9 state are contacted, either alone or admixed, or otherwise
10 incorporated with a metal or metals-containing solution,
11 or solutions, and thereby impregnated by either the
12 "incipient wetness" technique, or a technique embodying
13 absorption from a dilute or concentrated solution, or solu-
14 tions, with subsequent filtration or evaporation to effect
15 total uptake of the metallic components.

16 The Group VIII noble metal component is supported
17 on the carrier within a range which will provide, on the
18 finished catalyst composite, a concentration of from about
19 0.01 to 3 percent, preferably from about 0.2 to about 1
20 percent, based on the weight of the composite catalyst
21 (dry basis) exclusive of the added magnetic alloy com-
22 ponent. In compositing the metals with the carrier,
23 essentially any soluble compound can be used, but a soluble
24 compound which can be easily subjected to thermal decomposi-
25 tion and reduction is preferred, for example, inorganic
26 salts such as halide, nitrate, inorganic complex compounds,
27 or organic salts such as the complex salt of acetylacetone,
28 amine salt, and the like. Where, e.g., the Group VIII
29 noble metal is platinum, platinum chloride, platinum nitrate,
30 chloroplatinic acid, ammonium chloroplatinate, platinum
31 polyamine, platinum acetylacetonate, and the like, are
32 preferably used. The promoter metal, when employed, is
33 added in concentration which will provide, on the finished
34 catalyst composite, a concentration ranging about 0.01
35 to 3 percent, preferably from about 0.05 to about 1 percent,
36 based on the weight of the composite catalyst (dry basis),
37 exclusive of the magnetic component.

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1 The catalyst is dried by heating at a temperature
 2 above about 80°F, preferably between about 150°F and 300°F, in
 3 the presence of nitrogen or oxygen, or both, in an air
 4 stream or under vacuum. The catalyst is calcined at a
 5 temperature between about 500°F to 1200°F, preferably
 6 about 500°F to 1000°F, either in the presence of oxygen
 7 in an air stream or in the presence of an inert gas such
 8 as N₂.

9 The catalyst, if not sufficiently small, is
 10 preferably ground or crushed to a particulate mass of
 11 small particle size. A portion of the catalyst, is then
 12 admixed or otherwise dispersed with the particulate
 13 magnetic alloy and inorganic oxide precursor, suitably
 14 in the following proportions, based on the weight of the
 15 finished composite (dry basis), to wit:

	Inorganic Oxide Catalytic Metal-Containing Component Wt. %	Inorganic Oxide Gel Precursor Component, Wt. %	Particulate Magnetic Alloy Component, Wt. %
16 Typical	10-40	10-40	20-60
17 Preferred	25-35	25-35	30-50

18 A halide is added to the composite to enhance
 19 catalyst performance. Fluorine and chlorine are preferred
 20 halogen components. The halogen is contained on the
 21 catalyst within the range of 0.1 to 3 percent, preferably
 22 within the range of about 0.3 to 2 percent, based on the
 23 weight of the catalyst. When using chlorine as a halogen
 24 component, it is contained on the catalyst within the range
 25 of about 0.2 to 2 percent, preferably within the range of
 26 about 0.5 to 1.5 percent; based on the weight of the
 27 catalyst. The introduction of halogen into catalyst can
 28 be carried out by any method and at any time of the cata-
 29 lyst preparation, for example, prior to, following or
 30 simultaneously with the impregnation. In the usual opera-
 31 tion, the halogen component is introduced simultaneously
 32 with the incorporation of the metal hydrogenation-
 33 dehydrogenation component. It can also be introduced
 34 by contacting a carrier material in a vapor phase or

1 liquid phase with a halogen compound such as hydrogen
2 fluoride, hydrogen chloride, ammonium chloride, or the
3 like.

4 A sulfur component may be added. The sulfur con-
5 tent of the catalyst, if employed, will generally range
6 to about 0.2 percent, or more generally from about 0.02
7 percent to about 0.1 percent, based on the weight of the
8 catalyst (dry basis). The sulfur can be added to the cata-
9 lyst by conventional methods, suitably by breakthrough
10 sulfiding of a bed of the catalyst with a sulfur-containing
11 gaseous stream, e.g., hydrogen sulfide in hydrogen, per-
12 formed at temperatures ranging from about 350°F to about
13 1050°F and at pressures ranging from about 1-40 atmospheres
14 for the time necessary to achieve breakthrough, or the
15 desired sulfur level.

16 The catalyst composites of this invention may be
17 in the form of powder, beads, tablets, pills, spheres,
18 pellets or extrudates. The feed or charge stock can be a
19 virgin naphtha, cracked naphtha, a Fischer-Tropsch naphtha,
20 or the like. Typical feeds are those hydrocarbons contain-
21 ing from about 5 to 12 carbon atoms, or more preferably
22 from about 6 to about 9 carbon atoms. Naphthas, or
23 petroleum fractions boiling within the range of from
24 about 80°F to about 450°F, and preferably from about 125°F
25 to about 375°F, contain hydrocarbons of carbon numbers
26 within these ranges. Typical fractions thus usually con-
27 tain from about 15 to about 80 Vol. % paraffins, both
28 normal and branched, which fall in the range of about C₅
29 to C₁₂, from about 10 to 80 Vol. % of naphthenes falling
30 within the range of from about C₆ to C₁₂, and from 5 through
31 20 Vol. % of the desirable aromatics falling within the
32 range of from about C₆ to C₁₂.

33 The reforming runs are initiated by adjusting
34 the hydrogen and feed rates, and the temperature and pres-
35 sure to operating conditions. The run is continued at
36 optimum reforming conditions by adjustment of the major
37 process variables, within the ranges described below:

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1 Major Operating	Typical Process	Preferred Process
2 <u>Variables</u>	<u>Conditions</u>	<u>Conditions</u>
3 Pressure, Psig	50-750	100-300
4 Reactor, Temp., °F	900-1200	950-1050
5 Recycle Gas Rate, SCF/B	1000-10,000	1500-3000
6 Feed Rate, W/Hr/W	0.5-10	2.5-5
7 Methods of regeneration, and reactivation of		
8 these catalyst are conventional per se and form no part		
9 of the present invention. Reference is made, e.g. to		
10 Column 8, lines 47-68; Column 9, lines 1-68; and Column		
11 10, lines 1-10 of U.S. 4,125,455 by K.R. Clem et al which		
12 describes acceptable procedures; these portions of this		
13 patent being herewith incorporated by reference. Conven-		
14 tionally, an isolated reactor which contains a bed of		
15 catalyst, the latter having reached an objectionable degree		
16 of deactivation due to coke deposition thereon, is first		
17 purged of hydrocarbon vapors with a nonreactive or inert		
18 gas, e.g., helium, nitrogen, or flue gas. The coke or		
19 carbonaceous deposits are then burned from the catalyst		
20 by contact with an oxygen-containing gas at controlled		
21 temperature below the sintering point of the catalyst,		
22 generally below about 1300°F, and preferably below about		
23 1200°F.		
24 The agglomerated metals of the catalyst are re-		
25 dispersed and the catalyst reactivated by contact of the		
26 catalyst with halogen suitably a halogen gas or a substance		
27 which will decompose in situ to generate halogen. The gas		
28 is generally introduced as halogen, or halogen-containing		
29 gaseous mixture, into the reforming zone and into contact		
30 with the catalyst at temperatures ranging from about 550°F		
31 to about 1150°F, and preferably from about 700°F to about		
32 1000°F. The introduction may be continued up to the point		
33 of halogen breakthrough, or point in time when halogen is		
34 emitted from the bed downstream of the location of entry		
35 where the halogen gas is introduced. After redispersing		
36 the metals via the halogen treatment, the catalyst can		
37 then be rejuvenated by soaking in an admixture of air which		

1 contains about 6 wt. percent oxygen, at temperatures
2 ranging from about 850°F to about 950°F. Oxygen is then
3 purged from the reaction zone by introduction of a non-
4 reactive or inert gas, e.g., nitrogen, helium or flue
5 gas, to eliminate the hazard of a chance explosive combina-
6 tion of hydrogen and oxygen. A reducing gas, preferably
7 hydrogen or a hydrogen-containing gas generated in situ or
8 ex situ, is then introduced into the reaction zone and
9 contacted with the catalyst at temperatures ranging from
10 about 400°F to about 1100°F, and preferably from about
11 650°F to about 950°F, to effect reduction of the metal
12 hydrogenation-dehydrogenation components, contained on
13 the catalysts.

14 The invention will be more fully understood by
15 reference to the following simulated data illustrating its
16 more salient features. All parts are given in terms of
17 weight except as otherwise specified.

18 In the following examples a magnetic catalyst of
19 the present invention (Catalyst A) is prepared and its
20 performance compared in actual reforming runs with two
21 conventional non-magnetic catalysts (Catalysts B and C).
22 Additionally, the performance of Catalyst A in a reforming
23 run at similar conditions is compared with magnetic
24 catalysts (Catalysts D and E), similar to Catalyst A in all
25 respects except that the catalytic metal of the catalysts
26 was not redispersed after it had become agglomerated in
27 preparation.

28 EXAMPLES

29 Catalyst Preparation

30 Catalyst A, the catalyst of the present invention,
31 was prepared as follows:

32 A precalcined <400 mesh (Tyler) spray dried re-
33 forming grade alumina was impregnated with an H_2PtCl_6-HCl
34 solution in amount sufficient to provide nominally 0.6%
35 Pt and 1.5% chloride on the alumina. The catalyst was
36 then dried and calcined. Equal weight portions, on a dry
37 weight basis, of the impregnated alumina and an alumina

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1 gel were spray dried together at 900°F with a 410 stainless
2 steel powder, the catalyst obtained from the spray drier
3 being of the following composition, to wit:

4 30 wt.% pre-impregnated Al_2O_3 ,
5 30 wt.% non-impregnated Al_2O_3 ,
6 40 wt.% 410 stainless steel powder.

7 A portion of the spray dried catalyst was then
8 calcined at 900°F, and then treated to redisperse the aggro-
9 merated platinum component. The catalyst was thus heated
10 to 975°F in a 6% O_2 /94% N_2 gas stream over a 2-3 hour period,
11 and then held at this temperature for an additional 1/2
12 hour; then treated for 1/2 hour with a gas stream of 93.5%
13 N_2 /6% O_2 /0.5% Cl_2 ; and then held at 975°F in a 94% N_2 /6% O_2
14 gas stream for 2 hours, and then reduced to ambient tempera-
15 ture.

16 The catalyst was then reduced in hydrogen at 900°F,
17 and then tested in a fixed bed pilot plant reforming reactor
18 charged with 5 to 10 grams of the catalyst.

19 Four additional catalysts were prepared:

20 Catalysts B and C were prepared for use as control
21 catalysts. These catalysts are both non-magnetic (i.e.,
22 contain no magnetic particles), but in all other respects
23 are similar to Catalyst A. The platinum contained on the
24 catalyst is well dispersed.

25 Catalysts D and E, also magnetic catalysts, were
26 prepared. These catalysts are similar, and were prepared
27 in similar manner to Catalyst A except that the platinum
28 redispersion steps were omitted.

29 Reforming Runs

30 These catalysts were each then charged into a
31 reactor, and therein the catalysts are heated to reaction
32 temperature by a descending, hydrogen-hydrocarbon mixture.

33 A light Arabian paraffinic virgin naphtha feed
34 having the inspections given in Table I was charged downflow
35 with hydrogen into a reactor, to wit:

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TABLE I

1		
2	<u>ASTM Distillation, °F</u>	
3	Initial	183
4	5	213
5	10	220
6	30	238
7	50	262
8	70	288
9	90	317
10	95	326
11	Final B.P.	360
12	Gravity, °API	60.0
13	<u>Analysis, Vol.Percent</u>	
14	Paraffins	69.0
15	Naphthenes	18.1
16	Aromatics	12.9

17 Reforming, in each run, was carried out at condi-
18 tions required to produce a 100 RON product- i.e., at 950°F
19 EIT (average), 100 psig (average), and 4800 SCF/Bbl (aver-
20 age). The aromatics content of each product was measured,
21 since it is not possible to obtain an octane measurement
22 with a knock engine, and product octane was estimated from
23 a correlation based on reforming this same feed in a larger
24 pilot plant; this value being given in terms of a catalyst
25 performance number. The catalyst performance number (CPN)
26 is an index that includes activity, octane producibility and
27 process conditions.

28 Following a 1.5 hour line out period, four balance
29 periods were taken at 1.5 hour intervals and the data plotted
30 to determine the performance of each catalyst at the seventh
31 hour on oil for comparison purposes.

32 The results of these tests are given in the
33 Table II below.

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TABLE II
950°F, 100 psig, 4800 SCF/B

<u>Catalyst</u>	<u>Activity CPN @ Hour 7</u>	<u>C₅+Yield, LV% 100 RON @ Hour 7</u>
A	125	77.5
B	125	78.9
C	120	78.0
D	45	70.9
E	60	72.3

These data show that the performance of Catalyst A closely approximates that obtained by Catalysts B and C. The performance of Catalysts D and E, however, is quite poor. This is because the platinum dispersed on the alumina catalyst support is highly agglomerated as contrasted with that contained on Catalyst A. The high metals agglomeration, which occurred on Catalysts D and E during the spray drying step, causes considerably diminished activity and lower C₅+ liquid yield than Catalyst A.

It is apparent that various modifications or changes can be made, as in the temperature, solution concentration, and the like, without departing from the spirit and scope of the invention.

In this patent specification, the following conversions of units apply:

Temperatures expressed in °F are converted to °C by subtracting 32 and then dividing by 1.8.

Lengths expressed in inches (") are converted to cms by multiplying by 2.54.

Gas volumes expressed in standardized cubic feet (SCF) are converted to litres by multiplying by 28.32.

Liquid volumes expressed in barrels (B) are converted to litres by multiplying by 159.0.

Pressures expressed in pounds per square inch (psi) are converted to kg/cm^2 by multiplying by 0.07031.

CLAIMS

1. A method for the preparation of a catalyst suitable for use in a process for reforming a hydrocarbon feed in a reforming zone at reforming conditions wherein a bed of fluidizable, magnetizable catalytic particles is contacted and fluidized with a hydrocarbon feed and hydrogen while simultaneously subjected to an applied magnetic field, and a product of improved octane is withdrawn from said reforming zone, the method being characterized by:-

incorporating at least one Group VIII noble metal within an inorganic oxide particulate mass;

admixing said Group VIII metal-containing inorganic oxide particulate mass with magnetic alloy particles and an inorganic oxide precursor which serves as a binder;

forming a particulate composite mass comprising particles of magnetic alloy dispersed as inclusions within an inorganic oxide matrix; and then

drying and calcining said composite mass.

2. The method of claim 1 wherein the Group VIII noble metal is comprised of platinum.

3. The method of claim 1 or claim 2 wherein the composition of the dried calcined composite, based on the weight of the composite, is as follows:

from 10% to 40% of the inorganic oxide/Group VIII noble metal component,

from 20% to 60% of the magnetic alloy particles component, and

from 10% to 40% of the inorganic oxide component, added as a gel precursor.

4. The method of any one of claims 1, 2 or 3 wherein the particulate composite is of the following approximate composition:

the inorganic oxide/Group VIII noble metal component ranges from 25% to 35%,

the magnetic alloy particles component ranges from 30% to 50%,
and

the inorganic oxide component added as a gel precursor ranges from 25% to 35%.

5. The method of any one of claims 1, 2, 3 or 4 wherein the magnetic alloy particles are comprised of iron or cobalt.

6. The method of any one of claims 1 to 5 wherein the inorganic oxide component of the inorganic oxide portion of the particulate mass is principally alumina.

7. The method of any one of claims 1 to 6 wherein the Group VIII noble metal is incorporated in the metals-containing inorganic oxide particulate mass by impregnation.

8. The method of any one of claims 1 to 7 wherein the inorganic oxide particulate mass is of average particle size in the range of from 1 micron to 150 microns.

9. A catalyst suitable for use in a process for reforming a hydrocarbon feed in a reforming zone at reforming conditions when made by the method of any one of claims 1 to 8.

10. A process for reforming a hydrocarbon feed in a reforming zone at reforming conditions wherein a bed of fluidizable, magnetizable catalyst particles according to claim 9 is contacted and fluidized with a hydrocarbon feed and hydrogen while simultaneously being subjected to an applied magnetic field, and withdrawing a product of improved octane qualities from the reforming zone.

0031700



European Patent
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EUROPEAN SEARCH REPORT

Application number

EP 80 30 4646

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<u>US - A - 4 136 016</u> (ROSENSWEIG)		B 01 J 37/00 37/04 C 10 G 35/14 35/085
A	<u>FR - A - 2 387 078</u> (EXXON)		
A	<u>US - A - 3 143 511</u> (BICHARD et al.)		
A	<u>GB - A - 951 344</u> (ENGELHARD)		
A	<u>GB - A - 1 459 779</u> (EXXON)		
-----			TECHNICAL FIELDS SEARCHED (Int. Cl.)
			B 01 J 37/00 37/04 8/42 C 10 G 35/14 35/085
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 05-03-1981	Examiner MICHIELS